



Full Length Article

Synthesis and characterization of glycolate precursors to MTiO_3 ($\text{M} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$)

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ABSTRACT

Novel glycolate precursors to metal titanates MTiO_3 ($\text{M} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$) were synthesized by heating metal acetate and titanium isopropoxide in ethylene glycol up to 190 °C during distilling the water to avoid hydrolysis of precursors. These glycolate precursors were characterized by X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FT-IR), thermal analysis (TG-DTA), and scanning electron microscopy (SEM). The obtained three isostructural glycolate precursors were containing metal (Ni, Co, Zn), titanium, and ethylene glycol with a ratio of 1:1:4. The crystal growth processes of three precursors were different from each other. These precursors revealed homogeneous and well-defined rod-like structure with 0.5–3.0 μm in thickness and 4–20 μm in length. The obtained metal titanates were consisted of microrods with 0.4–1.5 μm in thickness and 2–15 μm in length.

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1. Introduction

NiTiO_3 and CoTiO_3 , which possess the ilmenite structure, are well known as functional inorganic materials with wide applications in electrodes of solid oxide fuels cells and gas sensors [1,2]. Zinc titanate has various polymorphs, such as cubic defect spinel $\text{Zn}_2\text{Ti}_3\text{O}_8$, cubic inverse spinel ZnTiO_3 , hexagonal ilmenite type ZnTiO_3 , and cubic inverse spinel Zn_2TiO_4 . Zinc titanates have attracted considerable attention for use as sorbents for desulfurization of coal gas, catalysts in liquid phase organic transformations, dielectric and microwave resonators, gas sensors, oxidation of hydrocarbons or CO and NO reduction, semiconductor materials, photocatalytic materials, and as pigments in paints [3–9].

In conventional solid-state reactions, the preparation of metal titanate powders requires long-duration heat treatment at a temperature of over 1000 °C until intermediate phases disappear. The synthesized granular powders are large and variant, and sometimes contain starting materials and generated byproducts. The pure ZnTiO_3 phase cannot be prepared from an equimolar mixture of ZnO and TiO_2 because the compound decomposes into Zn_2TiO_4 and is rutile at 945 °C [10].

Many different methods have been reported for the synthesis of crystalline NiTiO_3 powders, such as the sol-gel technique, the flux method, co-precipitations, and the Pechini process [11–14]. Recently, mesoporous ilmenite NiTiO_3 nanorods were synthesized by a facile sonochemical approach combined with a thermal treatment in air [15]. The syntheses of the heterobimetallic complex precursors $[\text{Ni}_2\text{Ti}_2(\text{OEt})_2(\text{l-OEt})_6(\text{acac})_4]$ (acac = 2,4-pentanedionate) and $[\text{M}(\text{H}_2\text{O})_5]_2[\text{Ti}_2(\text{O}_2)_2\text{O}(\text{nta})_2] \cdot 7\text{H}_2\text{O}$ [$\text{M} = \text{Co}, \text{Ni}, \text{and Zn}$] (H_3nta = nitrilotriacetic acid) by simple chemical techniques have also been reported [16,17].

The synthesis of heterobimetallic complex precursors is of considerable interest, for the following reasons:

- (1) The ratio of the two metals is preserved after calcination of the precursor
- (2) The uniformity and micro crystalline shape of the precursor are preserved
- (3) The oxide phase is obtained by heating at relatively low temperature
- (4) The oxide phase obtained by heating shows a single phase without a second phase

In this work, the synthesis of heterobimetallic complex precursors was attempted using the polyol method.

The polyol method is well known as a common and facile approach. Initial studies on the polyol method focused on the preparation of elemental metals and alloys by using the reducing properties of a high-boiling alcohol (i.e., glycerol or glycol).

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The alcohol often acts as a stabilizing agent that effectively limits its particle growth and hinders aggregation. The process is effective because of its self-seeding mechanism and the lack of a requirement for templating materials. The consequent low costs and ease of processing [18,19] make it an ideal process for potential industrial scale-up.

Over the past several years, the number of oxide material systems synthesized via the polyol method has steadily increased; several reports have summarized the polyol method as a sol-gel process carried out at elevated temperature that is suitable for the preparation of a host of binary and ternary oxides [20]. Ethylene glycol (EG) is one of the most widely used solvents for the polyol synthesis and the glycothermal method – the polyol process using EG as a solvent – has been utilized for the synthesis of a wide range of metal oxide materials [21]. In this case, a small amount of water proceeds the reaction. Several investigations have considered the role of the inorganic species in controlling the shape of metal and metal oxide microparticles, which may provide as strong an effect as organic surfactants, and the role of the polymers in controlling the shape of the synthesized microparticles [22,23]. For example, hexagonal thin sheet-like structured $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ crystallites were successfully synthesized in isopropyl alcohol [24].

Ethylene glycol (EG) is an important solvent for the polyol synthesis of metal and metal oxide microparticles due to its strong reducing capability, relatively high boiling point (197 °C), and high dielectric constant, which increases the solubility of inorganic salts [25,26]. EG is commonly used as a cross-linking reagent because of its propensity to coordinate to the central metal ion and form a metal glycolate, leading to subsequent oligomerization [27]. At first, EG acts as a solvent for the starting compound due to its rather high dielectric constant. Subsequently, it reduces the metal ion species in the liquid phase, in which nucleation and growth of the metallic phase occur. Thus, EG also acts as a crystal growth medium for the metal particles [28].

Several transition metal-EG compounds have been prepared. Microrods and microtubes composed of the Ni-EG complex have been fabricated selectively by adjusting the reaction temperature for synthesizing $\beta\text{-Ni}(\text{OH})_2$ microtubes [29]. A cobalt alkoxide, $\text{Co}(\text{OCH}_2\text{CH}_2\text{O})$, has been prepared from the reaction of cobalt acetate with EG. This compound crystallized as disk-shaped particles with diameters and width in the 0.4–1 mm and 100–250 nm ranges, respectively [30]. A simple and versatile solvent-growth process using EG has been demonstrated for the synthesis of novel faceted bipyramidal zinc glycolate [31]. Single crystals of the titanium glycolate complex $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ with a unique one-dimensional structure have been synthesized using hydrothermal methods. The structure is described as parallel chains built up from edge-sharing Ti^{4+}O_6 octahedra. The six oxygen atoms are offered by four EG ligands. Each EG ligand bridges two titanium atoms with one of its oxygen atoms, and the other is terminal [32].

With the aim of demonstrating a new route to the formation of metal titanates, the syntheses of heterobimetallic precursors conducted in the presence of EG are presented here. These novel precursors have been isolated and characterized by XRD, TG-DTA, FT-IR, and SEM. The chemical transformations from the precursors to metal titanates by heating in air were examined through crystal structure and crystalline morphology.

2. Experimental

2.1. Preparation of metal ($M = \text{Ni}^{2+}$, Co^{2+} , Zn^{2+}) titanate precursors

All chemicals were purchased from Wako Pure Chemical Reagent Co. and used as received without any purification. For the prepara-

tion of nickel titanate (Ni-Ti) precursors, a typical synthesis process was as follows: 2.48 g of nickel acetate ($(\text{CH}_3\text{COO})_2\text{Ni} \cdot 4\text{H}_2\text{O}$) and 50 ml of EG in a 100 ml round-bottom flask was heated to 52 °C until complete dissolution and then cooled to room temperature. Titanium isopropoxide ($\text{Ti}(\text{OiPr})_4$, 2.84 ml) was added under vigorous stirring. The as-formed green transparent solution was heated at a constant rate – 10 °C/min – while distilling off the water formed and stirring. The water distillation was adopted to avoid the hydrolysis of products. The solution suddenly became turbid at 173 °C and was then held at that temperature for 2 h. After cooling to room temperature, the product was separated by centrifugation and washed several times in acetone and then air dried at 60 °C. The syntheses of the cobalt and zinc titanate (Co-Ti and Zn-Ti) precursors were performed in the same manner as the Ni-Ti precursor by using cobalt and zinc acetate ($(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$).

2.2. Characterization

The phase identifications of the products were analyzed by means of X-ray diffraction (XRD, Rigaku UltimaIV) using $\text{Cu K}\alpha$ radiation. The ethylene glycol functional groups in the metal titanate precursors were characterized by FT infrared spectroscopy (FT-IR, JASCO FT/IR – 6510) using KBr pellets. The thermogravimetric and differential thermal analysis (TG-DTA) was performed in a TG/DTA 6300 SII EXSTAR 6000 thermal analysis system with a heating rate of 10 °C/min from 20 to 600 °C in air. The morphologies of products were observed using a scanning electron microscope (SEM) (JEOL JSM – 6510).

3. Results and discussion

3.1. Formation process of metal titanates

The as-formed green transparent solution was heated while being stirred in order to prepare NiTiO_3 precursor. The solution suddenly became turbid at 173 °C and was then held at 173 °C for 2 h. The products obtained at 173 °C (Figs. 1(a) and 2(a)) and after being held at this temperature for 2 h (Figs. 3 and 4(a)) possessed the same light blue color and XRD patterns and differed in morphology. The product obtained in the initial stage was similar to cylinders of 1–3 μm width and 2–8 μm length, but the crystalline micro-rods obtained after 2 h were clearly shrinking, exhibiting a 1–2 μm width and a 5–10 μm length and a partially hollow structure. Studies about the growth of the hollow structure are now in progress. As an initial analysis, the change of the cylindrical crystal to shrinking crystalline microrods after 2 h suggests a self-dissolution and precipitation process.

The product obtained after 2 h was calcined in air at 600 °C. Its characteristic XRD peaks (Fig. 5(a)) could be attributed to the reflections for ilmenite NiTiO_3 (rhombohedral structure; JCPDS No. 33-0960). No characteristic peaks of impurities such as TiO_2 and NiO were detected, indicating that the product was pure ilmenite NiTiO_3 . The strong and narrow diffraction peaks reveal its high crystallinity. Further decreased crystalline sizes of 0.5–1 μm in width and 1–4 μm in length are observed in the SEM (Fig. 6(a)), but the crystalline shape was preserved.

The as-formed deep purple transparent solution was heated while stirring to prepare CoTiO_3 precursor. The solution instantaneously became light purple and turbid at 190 °C. The products obtained at 190 °C (Figs. 1 and 2(b)) and after holding for 2 h (Figs. 3 and 4(b)) possess the same light blue color and XRD patterns and are clearly different in morphology.

The product obtained in the initial stage was a thin plate-like structure consisting of bundles of thin rods, 0.1–0.2 μm in width

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